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(11) Publication number : 0 609 081 A2

EUROPEAN PATENT APPLICATION

(12)

(21) Application number : 94300604.9

(51) Int. Cl.⁵ : H01L 21/3205

(22) Date of filing : 27.01.94

(30) Priority : 27.01.93 US 9521

(43) Date of publication of application :
03.08.94 Bulletin 94/31

(84) Designated Contracting States :
DE FR GB IT NL

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(54) Improved electrical connections to dielectric materials.

(57) A preferred embodiment of this invention comprises an oxidizable layer (e.g. tantalum 48), an oxygen gettering layer (e.g. platinum/tantalum mixture 34) overlaying the oxidizable layer, a noble metal layer (e.g. platinum 36) overlaying the oxygen gettering layer, and a high-dielectric-constant material layer (e.g. barium strontium titanate 38) overlaying the noble metal layer. The novel structures presented provide electrical connection to high-dielectric-constant materials without the disadvantages of current structures. The oxygen gettering layer controls oxygen diffusion, minimizing the formation of a resistive layer either in the lower electrode or at the lower electrode/substrate interface. The oxygen gettering layer acts as a gettering site for oxygen, where the oxygen oxidizes the reactive metal portion of the layer, leaving the noble metal portion of the layer intact. While the oxides/suboxides (e.g. tantalum pentoxide 40) that are formed are resistive, they are dispersed within the noble metal matrix, leaving a conductive path from the top of the layer to the bottom. This invention provides a stable and electrically conductive electrode for high-dielectric-constant materials while using standard integrated circuit materials to facilitate and economize the manufacturing process.

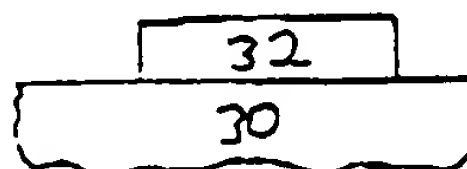


FIG. 1

EP 0 609 081 A2

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FIELD OF THE INVENTION

This invention generally relates to improving electrical connections to materials with high-dielectric-constants, such as in the construction of capacitors.

BACKGROUND OF THE INVENTION

Without limiting the scope of the invention, its background is described in connection with current methods of forming electrical connections to high-dielectric-constant materials, as an example.

The increasing density of integrated circuits (e.g. DRAMs) is increasing the need for materials with high-dielectric-constants to be used in electrical devices such as capacitors. The current method generally utilized to achieve higher capacitance per unit area is to increase the surface area/unit area by increasing the topography, such as in trench and stack capacitors using SiO_2 or $\text{SiO}_2/\text{Si}_3\text{N}_4$ as the dielectric. This approach becomes very difficult in terms of manufacturability for devices such as the 256 Mbit and 1 Gbit DRAMs.

An alternative approach is to use a high permittivity dielectric material. To be useful in electronic devices, however, reliable electrical connections should generally be constructed which do not diminish the beneficial properties of these high-dielectric-constant materials.

Heretofore, in this field, single and multiple metal layers are generally used to form electrical contacts to high-dielectric-constant materials. For example, to provide an electrical connection to a high-dielectric-constant material which makes up a capacitor on the surface of a semiconductor substrate, the following techniques are among those now employed: (a) dielectric/platinum/substrate, (b) dielectric/platinum/tantalum/substrate, and (c) dielectric/platinum/titanium/substrate. The layering sequence in these examples is from the top down to the substrate (e.g. silicon). A similar metallization scheme may be used for the top of the dielectric film to complete the capacitor structure.

SUMMARY OF THE INVENTION

According to one aspect of the present invention there is provided a method of forming a microelectronic structure, said method comprising forming an oxidizable layer; forming an oxygen gettering layer on said oxidizable layer which oxygen gettering layer getters diffusing oxygen, thus minimizing the formation of a oxidized resistive layer either in or on said oxidizable layer, forming a noble metal layer on said oxygen gettering layer; and forming a layer of a high-dielectric-constant material on said noble metal layer.

As used herein the term high-dielectric-constant (hereafter abbreviated HDC) means a dielectric constant greater than about 20. HDC materials are useful for the fabrication of many electrical devices, such as capacitors. However, HDC materials are generally not chemically stable when deposited directly on a semiconductor substrate, so one or more additional layers are required to provide the electrical connection between the HDC material and the substrate. The additional layer or layers should generally be chemically stable when in contact with the substrate and also when in contact with the high-dielectric-constant material.

Current methods provide for using platinum as the noble layer to contact the high-dielectric-constant material, along with tantalum or titanium as the sticking layer to contact the substrate. However, HDC materials (e.g. ferroelectrics) are generally deposited at elevated temperatures (greater than about 500°C) in an O_2 atmosphere. It has been discovered that, in this environment, oxygen diffuses through the platinum and forms a resistive layer of Ta_2O_5 or TiO_2 when it comes in contact with the Ta or Ti, causing high contact resistance. Further, the substrate (e.g. silicon) itself can become oxidized during the deposition of the HDC material. As used herein, the term oxidizable layer refers to the underlying sticking layer, or substrate, which becomes more insulating when oxidized.

The disclosed structures generally provide electrical connection to HDC materials without the disadvantages of the current structures. One embodiment of this invention comprises an oxidizable layer, an oxygen gettering layer overlaying the oxidizable layer, a noble metal layer overlaying the oxygen gettering layer, and a high-dielectric-constant material layer overlaying the noble metal layer. A method of forming an embodiment of this invention comprises the steps of forming an oxygen gettering layer on an oxidizable layer, forming a noble metal layer on the oxygen gettering layer, and forming a high-dielectric-constant material layer on the noble metal layer. Examples of processes for depositing the lower electrode materials are sputtering, evaporation, and chemical vapor deposition. Examples of processes for depositing the high-dielectric-constant material are ion-beam sputtering, chemical vapor deposition, and pulsed laser deposition.

These are apparently the first structures wherein an electrical connection to high-dielectric-constant materials comprises an oxygen gettering layer. The oxygen gettering layer controls oxygen diffusion, minimizing the formation of a resistive layer either in the oxidizable layer or at the oxidizable layer/oxygen gettering layer

interface. The oxygen gettering layer acts as a gettering site for oxygen, wherein the oxygen oxidizes the reactive metal portion of the layer, leaving the noble metal portion of the layer intact. While the oxides or suboxides that are formed are resistive, they are dispersed within the noble metal matrix, leaving a conductive path from the top of the layer to the bottom. The oxygen gettering layer should generally contain enough reactive metal to successfully combine with most or all of the diffused oxygen, but not so much that there is not a conductive path remaining via the noble metal component of the layer. Generally, the required thickness and composition of the oxygen gettering layer depend on the specific deposition parameters (temperature, O₂ pressure, etc.) of the high-dielectric-constant material. If enough oxygen reaches the oxidizable layer (e.g. the sticking layer or the substrate), a resistive layer will be formed, significantly increasing the contact resistance. The noble metal layer between the high-dielectric-constant material layer and the oxygen gettering layer is desirable, as it both minimizes undesirable reduction of the high-dielectric-constant material layer and lowers the amount of oxygen which enters the oxygen gettering layer. This invention generally provides a stable electrode for HDC materials while using standard integrated circuit materials to facilitate and economize the manufacturing process.

BRIEF DESCRIPTION OF THE DRAWINGS

The novel features believed characteristic of the invention are set forth in the appended claims. The invention itself, however, as well as other features and advantages thereof, will be best understood by reference to the detailed description which follows, read in conjunction with the accompanying drawings, wherein:

FIGS. 1-5 are cross-sectional views of a method for constructing a metal/high-dielectric-constant material/metal capacitor on a semiconductor substrate;
 FIGS. 6-9 are cross-sectional views of metal/high-dielectric-constant material/metal capacitors formed on the surface of a semiconductor substrate;
 FIG. 10 is a cross-sectional view of an intermediate structure, a lower electrode formed on the surface of a semiconductor substrate, before the deposition of a high-dielectric-constant material layer;
 FIG. 11 is a cross-sectional view of an oxygen gettering layer providing electrical connection between a high-dielectric-constant material layer and an oxidizable layer;
 FIG. 12 is a cross-sectional view of a metal/high-dielectric-constant material/metal capacitor formed on the surface of a semiconductor substrate; and
 FIG. 13 is a cross-sectional view of a lower electrode providing electrical connection between a high-dielectric-constant material and a semiconductor substrate.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

With reference to Figures 1-5, there is shown a method of forming a preferred embodiment of this invention, a capacitor comprising a high-dielectric-constant material and an oxygen gettering layer. Figure 1 illustrates a tantalum sticking layer 32 deposited on the surface of a semiconductor body 30. Figure 2 illustrates a platinum/tantalum mixture layer 34 deposited on the tantalum sticking layer 32. The ratio of platinum to tantalum in the platinum/tantalum mixture layer 34 is, in this example, between 3:1 and 1:1.5. A method of forming this oxygen gettering layer 34 involves depositing the platinum and tantalum in the same process chamber using two sputter guns, so that the desired percentages of each metal are deposited, forming a mixture of the two metals. Other processes such as evaporation or chemical vapor deposition could also be used to deposit the two metals. Figure 3 illustrates a platinum noble layer 36 deposited on the oxygen gettering layer 34. The three layers 32, 34, and 36 constitute the lower electrode of the capacitor. Figure 4 illustrates a barium strontium titanate layer 38 deposited on the platinum layer 36, and also the tantalum oxide particles 40 that are formed in the oxygen gettering layer 34 as a consequence of the barium strontium titanate layer 38 being deposited in a high temperature oxygen atmosphere. The lower electrode, comprising layers 32, 34, and 36, remains electrically conductive after the barium strontium titanate deposition since the oxide particles 40 are spread throughout the oxygen gettering layer 34. The barium strontium titanate layer 38 constitutes the dielectric of the capacitor. Figure 5 illustrates a titanium nitride layer 42 deposited on the barium strontium titanate layer 38, forming the upper electrode of the capacitor. Although Figure 5 illustrates a planar geometry for all of the elements of the capacitor, this invention applies equally well to the construction of capacitor structures of more complicated geometries, including capacitors built into depressions in the semiconductor surface.

In an alternate embodiment, with reference to Figure 6, such a capacitor structure may be formed without the tantalum layer 32 of Figure 5, and thus the oxygen gettering layer is preventing the oxidation of the top of the substrate. In another alternate embodiment, with reference to Figure 7, such a capacitor structure may

be formed without the platinum layer 36 of Figure 5. In another alternate embodiment, with reference to Figure 8, such a capacitor structure may be formed without either the tantalum layer 32 or the platinum layer 36 of Figure 5.

In another alternate embodiment, with reference to Figure 9, such a capacitor structure may be formed with a lower electrode comprising a graded layer 44 in which the amounts of each metal vary with respect to depth in the layer. The graded layer 44 is formed such that primarily tantalum is deposited near the semiconductor substrate, and then as the layer continues to be formed, the amount of platinum deposited is increased while the amount of tantalum deposited is decreased. Near the top of the layer, primarily platinum is deposited.

In another alternate embodiment, with reference to Figure 10, such a capacitor may be formed with a lower electrode comprising a stratified region 46 between the tantalum layer 32 and the platinum layer 36. This stratified region 46 comprises relatively thin alternating layers of platinum and tantalum, which will intermix when heated, dispersing the tantalum into the platinum. The number and thickness of the layers in the stratified region 46 can be varied, depending on the amounts of tantalum and platinum required. Figure 10 depicts the lower electrode before application of the HDC material.

In another alternate embodiment, with reference to Figure 11, the oxygen gettering layer 34 may be formed on an oxidizable layer 48. A platinum noble layer 36 is formed on the oxygen gettering layer 34, and a barium strontium titanate layer 38 is formed on the platinum layer 36, which causes the oxide particles 40 to form.

In another alternate embodiment, with reference to Figure 12, the tantalum sticking layer 32 may be formed on a titanium nitride barrier layer 52, which is itself formed on a titanium silicide contact layer 50. The titanium nitride layer 52 and titanium silicide layer 50 are formed by depositing a thin layer of titanium on the silicon substrate 30, and then annealing in an NH_3 atmosphere. The titanium silicide layer 50 forms a low resistance contact to the underlying silicon substrate 30, while the titanium nitride layer 52 prevents the formation of insulating tantalum silicide between the silicon substrate 30 and the tantalum sticking layer 32.

In yet another alternate embodiment, with reference to Figure 13, a tantalum plug 56 is formed through a silicon dioxide insulating layer 54, connecting the platinum/tantalum mixture layer 34 to the underlying silicon substrate 30.

The sole Table, below, provides an overview of some embodiments and the drawings.

Drawing Element	Generic Term	Preferred or Specific Examples	Other Alternate Examples
30	Semiconductor Substrate	Silicon	Other single component semiconductors (e.g. germanium) Compound semiconductors (e.g. GaAs, Si/Ge, Si/C) May be the oxidizable layer (e.g. if no sticking layer is used)
32	Sticking layer (when used, is generally the oxidizable layer)	Tantalum	Other reactive metals (e.g. tungsten, titanium, molybdenum). Reactive metal compounds (e.g. nitrides: titanium nitride, zirconium nitride; silicides: titanium silicide, tantalum silicide, tungsten silicide, molybdenum silicide; carbides: tantalum carbide; borides: titanium boride) Conductive carbides and borides (e.g. boron carbide)

5 10 15 20 25 30 35	34	Oxygen gettering layer	Platinum/ tantalum mixture wherein the ratio of platinum to tantalum is between 3:1 and 1:1.5	Noble metal/reactive metal mixtures wherein the ratio of noble metal to reactive metal is between 99:1 and 1:3 (e.g. other platinum/tantalum mixtures, platinum/tungsten mixtures, platinum/titanium mixtures) Noble metal/reactive metal compound mixtures wherein the ratio of noble metal to reactive metal compound is between 99:1 and 1:3 (e.g. platinum/titanium nitride mixtures) Other combinations of above mentioned materials (e.g. platinum/tantalum/tungsten mixture) Other combinations of materials selected from Drawing Element 32 above and Drawing Element 36 below (e.g. palladium/molybdenum mixtures)
40 45 50 55	36	Noble layer	Platinum	Other noble metals (e.g. palladium, rhodium, gold, iridium, silver)

38	High-dielectric-constant material	Barium strontium titanate	Other transition metal titanates, tantalates, niobates, and zirconates (e.g. barium titanate, strontium titanate, lead zirconate titanate, lead zinc niobate) Other high dielectric constant oxides (e.g. tantalum pentoxide)
40	Oxide particles	Tantalum pentoxide	Other oxides/suboxides of reactive metals and reactive metal compounds (e.g. other tantalum oxides, tungsten oxides, titanium oxides)
42	Upper electrode	Titanium nitride	Other metal nitrides Ruthenium dioxide $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ Noble metals (e.g. platinum, palladium, rhodium, gold, iridium, silver) Other common semiconductor electrodes (e.g. silicides, aluminum)

5	44	Graded layer	Platinum/ tantalum mixture wherein the mixture is 100% tantalum near the substrate and transitions to 100% platinum near the HDC material	Other noble metal/reactive metal mixtures wherein the mixture is 100% reactive metal near the substrate and transitions to 100% noble metal near the HDC material (e.g. platinum/tungsten mixture, platinum/titanium mixture) Noble metal/reactive metal compound mixtures wherein the mixture is 100% reactive metal compound near the substrate and transitions to 100% noble metal near the HDC material (e.g. platinum/titanium nitride mixture) Other combinations of above mentioned materials (e.g. platinum/ tantalum/tungsten mixture) Other combinations of materials selected from Drawing Element 32 above and Drawing Element 36 above (e.g. palladium/molybdenum mixtures)
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5	46	Stratified region	Alternating layers of platinum and tantalum wherein the thickness ratio of the platinum layers to the tantalum layers is between 3:1 and 1:1.5	Alternating layers of other noble and reactive metals wherein the thickness ratio of the noble metal layers to the reactive metal layers is between 99:1 and 1:3 (e.g. platinum/tantalum, platinum/tungsten, platinum/titanium) Alternating layers of noble metal and reactive metal compound wherein the thickness ratio of the noble metal layers to the reactive metal compound layers is between 99:1 and 1:3 (e.g. platinum/titanium nitride) Other combinations of above mentioned materials (e.g. platinum/tantalum/tungsten) Other combinations of materials selected from Drawing Element 32 above and Drawing Element 36 above (e.g. palladium/molybdenum)
10				
15				
20				
25				
30				
35				

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5	48	Oxidizable layer	Tantalum	Other reactive metals (e.g. tungsten, titanium, molybdenum) Reactive metal compounds (e.g. nitrides: titanium nitride, zirconium nitride; silicides: titanium silicide, tantalum silicide, tungsten silicide, molybdenum silicide; carbides: tantalum carbide; borides: titanium boride) Conductive carbides and borides (e.g. boron carbide) Single component semiconductors (e.g. single crystalline and polycrystalline silicon, germanium) Compound semiconductors (e.g. GaAs, Si/Ge, Si/C)
10				
15				
20				
25				
30	50	Contact layer	Titanium silicide	Other conductive silicides
	52	Barrier layer	Titanium nitride	Other conductive nitrides Other high-temperature conductive diffusion barriers
35	54	Insulator	Silicon dioxide	Other insulators (e.g. silicon nitride)

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56	Conductive Plug	Tantalum	Other reactive metals (e.g. tungsten, titanium, molybdenum) Reactive metal compounds (e.g. nitrides: titanium nitride, zirconium nitride; silicides: titanium silicide, tantalum silicide, tungsten silicide, molybdenum silicide; carbides: tantalum carbide; borides: titanium boride) Conductive carbides and borides (e.g. boron carbide) Single component semiconductors (e.g. single crystalline and polycrystalline silicon, germanium) Compound semiconductors (e.g. GaAs, Si/Ge, Si/C)
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A few preferred embodiments have been described in detail hereinabove. It is to be understood that the scope of the invention also comprehends embodiments different from those described, yet within the scope of the claims. With reference to the structures described, electrical connections to such structures can be ohmic, rectifying, capacitive, direct or indirect, via intervening circuits or otherwise. Implementation is contemplated in discrete components or fully integrated circuits in silicon, germanium, gallium arsenide, or other electronic materials families. In general the preferred or specific examples are preferred over the other alternate examples. Unless otherwise stated, all composition ratios or percentages are in relation to composition by weight. In some intermediate structures, and in the final product, the oxygen gettering layer will generally be at least partially oxidized.

While this invention has been described with reference to illustrative embodiments, this description is not intended to be construed in a limiting sense. Various modifications and combinations of the illustrative embodiments, as well as other embodiments of the invention, will be apparent to persons skilled in the art upon reference to the description. It is therefore intended that the appended claims encompass any such modifications or embodiments.

Claims

1. A method of forming a microelectronic structure, said method comprising:
 - forming an oxidizable layer;
 - forming an oxygen gettering layer on said oxidizable layer which oxygen gettering layer getters diffusing oxygen, thus minimizing the formation of a oxidized resistive layer either in or on said oxidizable layer;
 - forming a noble metal layer on said oxygen gettering layer; and
 - forming a layer of a high-dielectric-constant material on said noble metal layer.
2. The method according to claim 1, further comprising forming said oxygen gettering layer to be part of a final structure and least partially oxidized.

3. The method according to claim 1, further comprising forming said oxygen gettering layer to be part of an intermediate structure and not substantially oxidized.
4. The method according to any preceding claims, further comprising forming an electrically conductive layer on said high-dielectric-constant material layer.
5. The method according to claim 4, further comprising selecting said electrically conductive layer from the group consisting of: titanium nitride, ruthenium dioxide, $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, platinum, palladium, rhodium, gold, iridium, silver, and combinations thereof.
6. The method according to any preceding claim, further comprising forming said oxygen gettering layer comprising a mixture of at least one noble metal and at least one reactive component, wherein the ratio of said noble metal to said reactive component is between about 99:1 and about 1:3.
7. The method according to claim 6, further comprising forming oxygen gettering layer comprising said graded mixture of at least one noble metal and at least one reactive component, wherein said reactive component constitutes greater than 99% of said oxygen gettering layer near said oxidizable layer, and said reactive component transitions to constitute less than 1% of said oxygen gettering layer near said noble metal layer.
8. The method according to any preceding claim, further comprising forming said noble metal from the group consisting of: platinum, palladium, rhodium, gold, iridium, silver, and combinations thereof.
9. The method according to any of claims 6 to 8, further comprising selecting said reactive component and said oxidizable layer from the group consisting of: tantalum, tungsten, titanium, molybdenum, titanium nitride, zirconium nitride, titanium silicide, tantalum silicide, tungsten silicide, molybdenum silicide, tantalum carbide, titanium boride, boron carbide, silicon, germanium, carbon, GaAs, and combinations thereof.
10. The method according to any preceding claim, further comprising selecting said high-dielectric-constant material from the group consisting of: barium strontium titanate, barium titanate, strontium titanate, lead zirconium titanate, lead zinc niobate, tantalum pentoxide, and combinations thereof.
11. The method according to any preceding claim for forming a microelectronic capacitor layer.
12. A microelectronic structure comprising:
 - an oxidizable layer;
 - an oxygen gettering layer overlaying said oxidizable layer;
 - a noble metal layer overlaying said oxygen gettering layer; and
 - a layer of a high-dielectric-constant material overlaying said noble metal layer,
 whereby said oxygen gettering layer getters diffusing oxygen, thus minimizing the formation of an oxidized resistive layer either in or on said oxidizable layer.
13. The structure of claim 12, wherein said oxygen gettering layer is part of a final structure and is at least partially oxidized.
14. The structure of claim 12, wherein said oxygen gettering layer is part of an intermediate structure and is not substantially oxidized.
15. The structure of any of claims 12 to 14, wherein said structure further comprises an electrically conductive layer overlaying said high-dielectric-constant material layer.
16. The structure of any of claims 12 to 14, wherein said oxygen gettering layer comprises a mixture of at least one noble metal and at least one reactive component wherein the ratio of said noble metal to said reactive component is between about 99:1 and about 1:3.
17. The structure of claim 16, wherein said reactive component constitutes greater than 99% of said oxygen gettering layer near said oxidizable layer, and said reactive component transitions to constitute less than 1% of said oxygen gettering layer near said noble metal layer.

PATENT SKETCH FORM

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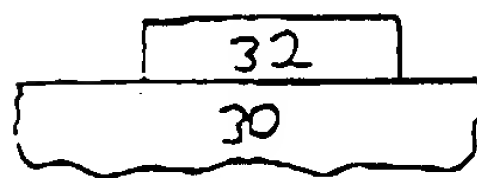


FIG. 1

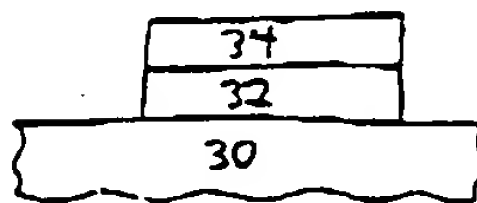


FIG. 2

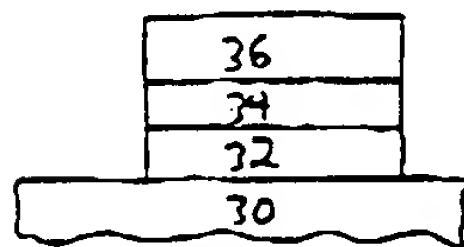


FIG. 3

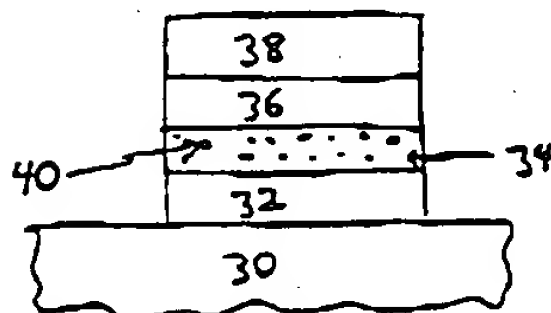


FIG. 4

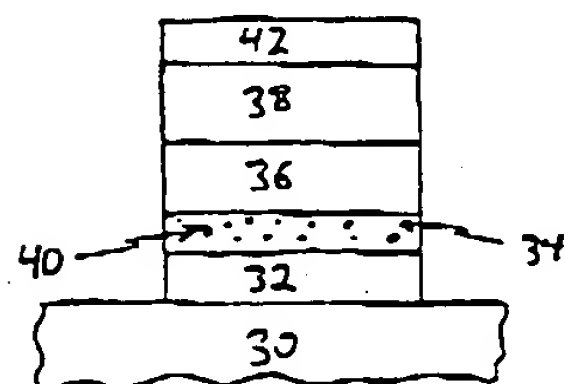


FIG. 5

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PATENT SKETCH FORM

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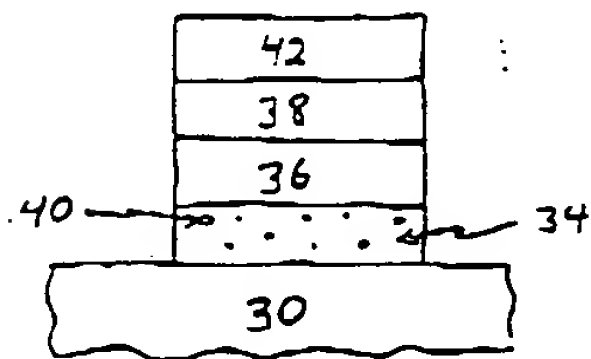


FIG. 6

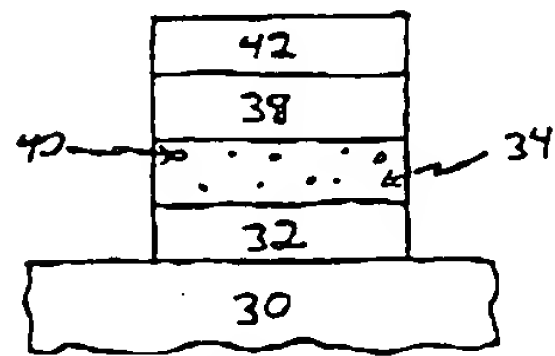


FIG. 7

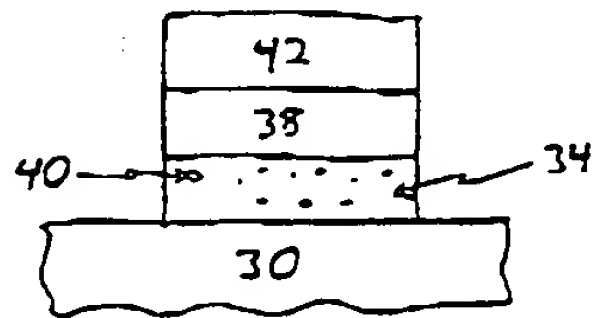


FIG. 8

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PATENT SKETCH FORM

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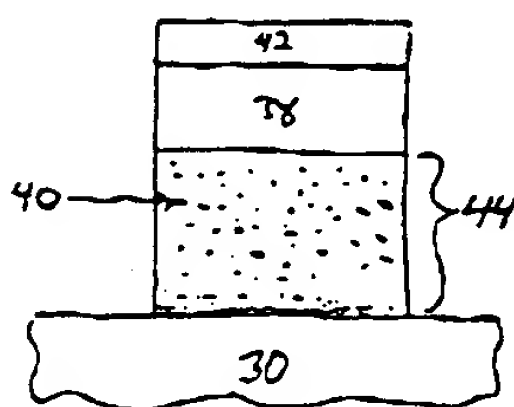


FIG. 9

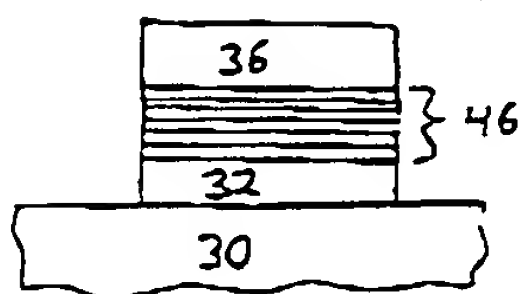


FIG. 10

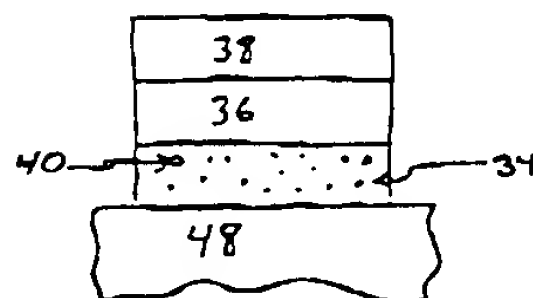


FIG. 11

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PATENT SKETCH FORM

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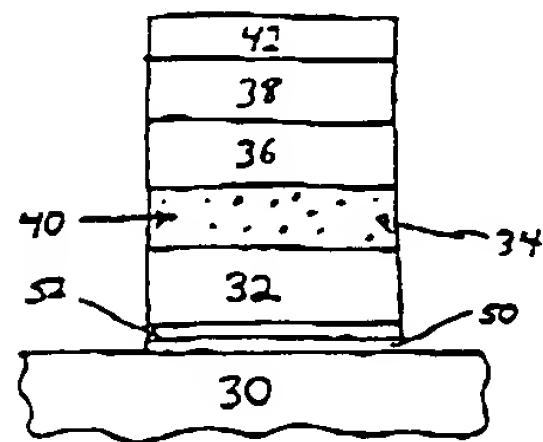


FIG. 12

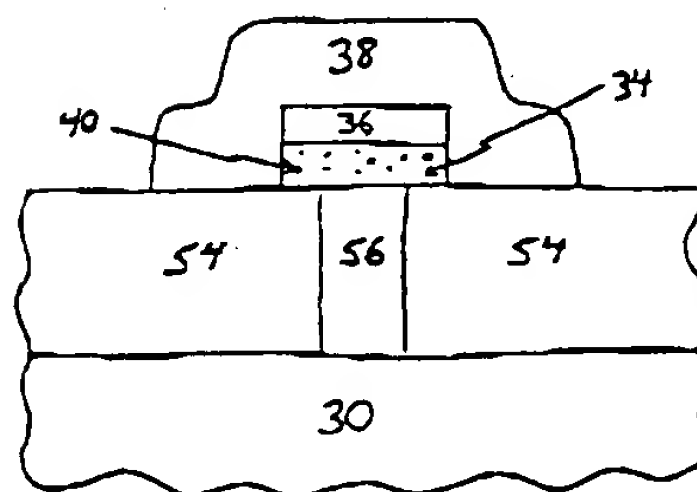
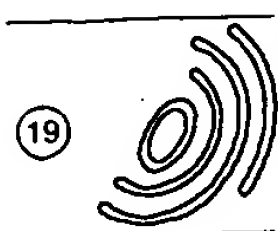
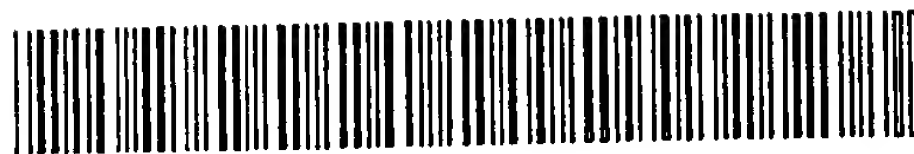


FIG. 13



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(11) Publication number : 0 609 081 A3

EUROPEAN PATENT APPLICATION

(12)

(21) Application number : 94300604.9

(51) Int. Cl.⁵ : H01L 21/3205

(22) Date of filing : 27.01.94

(30) Priority : 27.01.93 US 9521

(43) Date of publication of application :
03.08.94 Bulletin 94/31

(84) Designated Contracting States :
DE FR GB IT NL

(88) Date of deferred publication of search report :
08.03.95 Bulletin 95/10

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(54) Improved electrical connections to dielectric materials.

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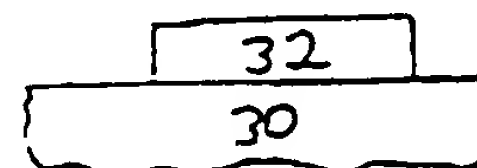


FIG. 1

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European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 30 0604

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. CL.5)
X	EP-A-0 404 295 (RAMTRON CORPORATION) * column 2, line 25 - column 3, line 36; figure 1 *	1,4,5,8, 9,11,12	H01L21/3205
X	INTERNATIONAL ELECTRON DEVICES MEETING TECHNICAL DIGEST 1991, 8 December 1991, WASHINGTON DC, US pages 823 - 826 K. KOYAMA ET AL. 'A stacked capacitor with (BaxSr1-x)TiO3 for 256M DRAM' * the whole document *	1,4-6, 8-12,15, 16	
A	EP-A-0 448 151 (N.V. PHILIPS' GLOEILAMPENFABRIEKEN) * the whole document *	1,4,5, 8-12,15	
A	US-A-5 164 808 (EVANS JR ET AL.) * the whole document *	1,4,5, 8-12,15	
A	EP-A-0 488 283 (NEC CORPORATION) * column 2, line 55 - column 3, line 50; figures 1A-1E *	1,4,5, 8-12,15	<div>TECHNICAL FIELDS SEARCHED (Int. CL.5)</div> <div>H01L</div>
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 20 December 1994	Examiner Baillet, B
<div>CATEGORY OF CITED DOCUMENTS</div> <div> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document </div> <div> T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document </div>			